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Efficient Ring-Opening Polymerization of a γ-Butyrolactone Derivative. First Anionic Double Ring-Opening Polymerization

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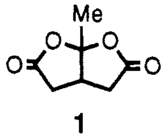
Introduction. Ring-opening polymerizations of lactones are well-known to afford corresponding polyesters in good yields.[1,2] However, generally five-membered lactones such as γ-butyrolactone do not polymerize to the corresponding polyesters at all.[1,2] Therefore, achievement of ring-opening polymerization of γ-butyrolactones is one of the important subjects in the field of polymer synthesis.[3-5] Two homopolymerizations of bicyclic γ-butyrolactones have been reported by Hall[4] and Okada,[5] but no high molecular weight polymer has been obtained. Copolymerizations of γ-butyrolactones with other lactones or cyclic ethers have been attempted so far, but no efficient introduction of the γ-butyrolactone unit has been accomplished.[6] In the course of our study on ring-opening polymerization of γ-butyrolactones, we recently examined anionic homopolymerization of a bicyclic bis(γ-butyrolactone) (1) but no corresponding polyester was obtained at all. Meanwhile, it was found that 1 copolymerized very efficiently with epoxides to afford the corresponding alternating copolymers (2) in good yields.[7] During the development of homopolymerizable monomers which contain a γ-butyrolactone structure, we have designed a spirocyclic γ-butyrolactone (3) as one potential candidate. In this paper, we describe the efficient ring-opening polymerization of this γ-butyrolactone derivative. This polymerization can also be regarded as the first anionic double ring-opening polymerization.



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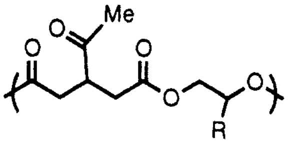

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Results and Discussion. The anionic polymerization of 3 (Scheme I)[8] with potassium *tert*-butoxide (5 mol %) was carried out at room temperature in tetrahydrofuran (THF) for 2 h.[9] Quantitative conversion of 3 was confirmed by ^{1}H NMR of the polymerization mixture. A gel permeation chromatograph (GPC) of the polymerization mixture indicated formation of a polymer with a number-average molecular weight ($\bar{M}_n$) of 9600. The polymer was isolated as a white powder by precipitation with methanol (yield 91%) (Table I, run 1). An IR spectrum of the polymer showed the absence of a lactone carbonyl absorption (1769 cm^{-1}) and the presence of an ester carbonyl absorption (1734 cm^{-1}). In the ^{1}H NMR spectrum multiplet signals corresponding to the benzylic methine protons were observed around 6.11 ppm with a reasonable integration ratio, other than those of aromatic (7.69–6.90 ppm) and the *tert*-butyl protons originating from the initiator (1.29 ppm) (Figure 1A). Therefore, the structure of the polymer was confirmed to be that of polyester 4 which might be formed via a double ring-opening polymerization with isomerization. In the ^{13}C NMR spectrum of the polymer neither the spiro carbon (124.3 ppm) nor the lactone carbon signal (167.0 ppm) was observed. On the other hand, the ester carbon signal appeared at 165 ppm, supporting the polyester structure of 4.

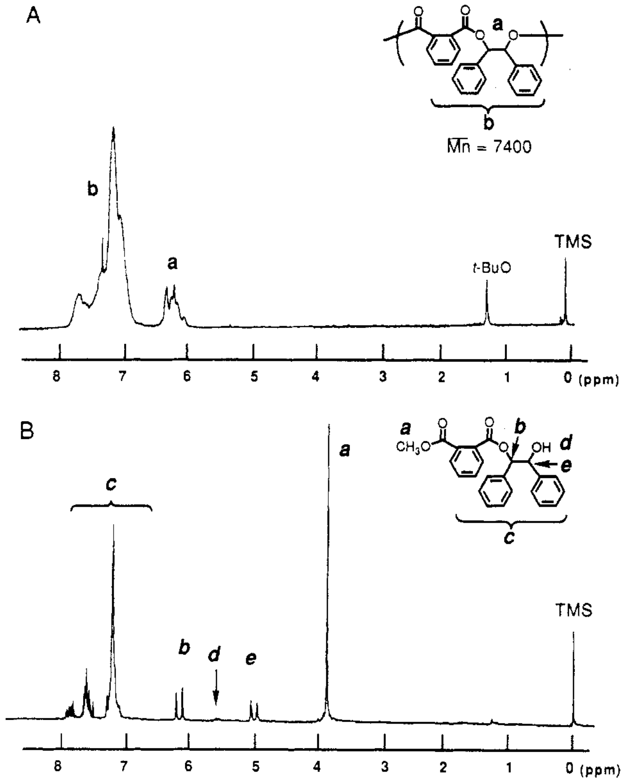


Figure 1. ^{1}H NMR spectra of polymer **4** ($\bar{M}_n$ = 9400) (A) and 1:1 adduct **5** (B) in $CDCl_3$.

Scheme I

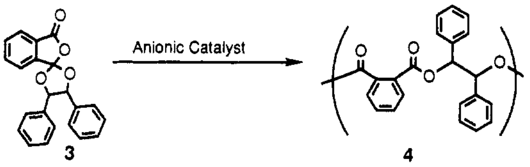
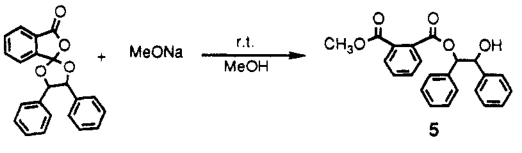


Table I
Anionic Polymerization of 3[a]

run. no.	initiator	THF (M)	temp (°C)	conv[b] (%)	yield[c] (%)	$\bar{M}_n(\bar{M}_w/\bar{M}_n)$[d]
1	*t*-BuOK	1.0	rt[e]	100	91	9600 (1.59)
2	*t*-BuOK	0.5	rt	100	76	6500 (1.56)
3	MeLi	1.0	0	100	90	7400 (1.13)
4	MeLi	1.0	rt	100	90	10000 (1.14)

[a] Polymerization conditions: monomer (0.5 mmol), initiator (5.0 mol %), 2 h. [b] Determined by ^{1}H NMR. [c] Methanol-insoluble polymer. [d] Estimated by GPC (based on PSt standards). [e] Room temperature.

Scheme II



A model reaction of 3 with an equimolar amount of sodium methoxide at room temperature for 15 min in methanol resulted in formation of a hydroxy ester (5; Scheme II) in 65% yield along with dimethyl phthalate (38 mol %) and 1,2-diphenylethyleneglycol (32 mol %) as the secondary products. The ^{1}H NMR spectrum of 5 showed signals due to benzylic protons adjacent to an ester

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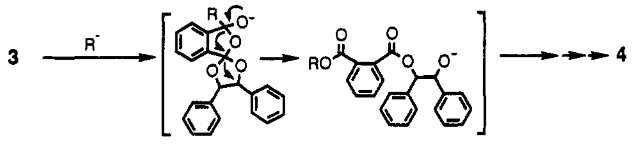
Scheme III



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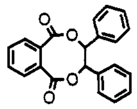

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oxygen at 6.16–6.07 ppm and aromatic protons at 7.85–7.15 ppm. The ^1H NMR spectra of 5 and 4 show considerable similarities which may be explained by a similar structure as proposed for 4.

From the above-mentioned results, we propose as a mechanism for the anionic polymerization of 3 to polyester 4 the tandem double ring-opening reaction involving an isomerization, as indicated in Scheme III.

Usually γ-butyrolactones show a quite low probability in view of homopolymerization, which is explained by a difference in rate constants in favor of recyclization to monomer versus ring-opening polymerization. The successful homopolymerization of the γ-butyrolactone derivative 3 might be explained by a reduced degree of "backbiting" caused by increased ring strain in the spirocyclic molecule. Furthermore, cyclization of the propagating species (7) to a cyclic diester (8), which can be assumed to be formed via an eight-membered ring as the transition state is expected to be disfavored for entropic reasons.[10] Judging from the NMR data, which show considerable incorporation in the polymer of *tert*-butyl end groups originating from the initiator, we can also rule out a significant formation of macrocycles via a backbiting mechanism (Figure 1A). If macrocycle formation, recyclization to the monomer or a cyclic diester, and chain transfer by the attack of another polymer chain occur on a negligible level, we can regard the polymerization to be a living nature. Methyllithium (MeLi) was chosen as the initiator because it reacts as a stronger nucleophile compared with potassium *tert*-butoxide; the lithium cation may suppress the transfer reaction to a greater extent than the potassium cation reacts as.

Anionic polymerization with MeLi under similar conditions proceeded efficiently to give polyesters 4 with narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.13–1.14) in high yields (Table I, runs 1 and 2). Furthermore, the polymerization showed a good linear relationship between $\bar{M}_n$ of 4 and the conversion of 3 (Figure 2). The $\bar{M}_n$ increased with an increase in the conversion of 3. These results appear to reveal a slow transfer reaction or backbiting in the polymerization of 3.

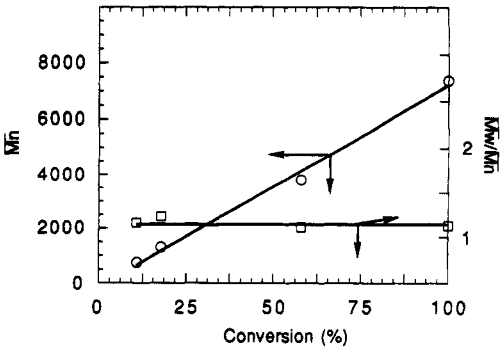

Figure 2. Relationship between $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of 4 vs conversion of spirocyclic γ-butyrolactone (3) in the polymerization of 3 with MeLi in THF at 0 °C.

Thus, we have succeeded in achieving anionic ring-opening polymerization of a spirocyclic γ-butyrolactone derivative (3), a monomer having a γ-butyrolactone skeleton, which efficiently polymerizes via tandem double ring opening with concurrent isomerization to yield the corresponding polyester (4).

References and Notes

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(9) The polymerization was carried out in a flask equipped with a three-way stopcock under argon atmosphere. To 3 (0.172 g, 0.5 mmol) in THF (0.5 mL) was added at room temperature a potassium *tert*-butoxide–THF solution (1.0 mol/L, 25 μL). The polymerization mixture was quenched by addition of acetic acid (1.5 mL of methylene dichloride solution, 1 vol %) and precipitated with 40 mL of methanol. The methanol-insoluble part was collected as a white powder (0.155 g, 90% yield).

(10) The eight-membered cyclic diester (8) can be obtained as a byproduct in the synthesis of 3.[8] When 8 was treated with *t*-BuOK (5 mol %) under similar conditions, the corresponding polyester with the same structure as 4 (the polymer of 3) was obtained. Therefore, 8 would not be found as a byproduct, if it could be formed during the polymerization. However, the living-like polymerization behavior of 3 seems to suggest that elimination of 8 is unlikely to occur.